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## MULTIPLE STAGE CROSS-CURRENT EXTRACTION USING VEGETABLE OIL IN THE REMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS-CONTAMINATED SOIL

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### Abstract

The present study aims to compare the efficiency of a single extraction and a 3-stage cross-current extraction of PAHs from both lowly contaminated (LC) and highly contaminated (HC) sands using palm kernel and soybean oils (PKO, SO). It is observed that 3-stage cross-current extractions increase the total efficiencies compared to single extractions by 18.7–22.7% and 27.2–30.6% for LC and HC sands, respectively. Maximum efficiencies of 94.3% and 98.4% are obtained for phenanthrene (PHEN) and fluoranthene (FLT), respectively using PKO at 70°C in the 3-stage cross-current extraction. In HC soil, these efficiencies reduce by 11.6% and 9.2% for PHEN and FLT, respectively. An oil flotation process as a post treatment step for soil/oil slurry is demonstrated to successfully remove 88.8–90.0 % residue oil from treated sand and 70.5–75.7 % residue oil from treated soil. Finally, a conceptual process of the extraction of PAHs from contaminated soil using vegetable oil is proposed.

**Keywords:** extraction, polycyclic aromatic hydrocarbons (PAHs), remediation, soil, vegetable oil

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a recalcitrant group of contaminants formed through pyrolytic processes or incomplete combustion of hydrocarbon fuels. Soil is the major repository for PAHs in which they reside within the non-aquatic phases and the soil organic matter (SOM) (Savic et al., 2016; Wild and Jones, 1995). Due to the toxicity of PAHs and the risks they pose to human health and the environment, remediation of PAH-contaminated sites is necessary in some countries before these sites can be reused. One commonly employed soil remediation technology is solvent extraction (Gan et al., 2009; Li et al., 2016). Solvent extraction which

involves the dissolution of PAHs from soil into an organic solvent phase can be applied to a large range of soil particle sizes since organic solvents provide better PAH selectivity than aqueous solutions (Hyman and Dupont, 2001).

Vegetable oil has recently been proposed as a non-toxic, biodegradable and cost-effective extracting agent for PAHs in contaminated soils (Yap et al., 2010). Laboratory-scale batch extractions of PAH-contaminated soil have been carried out using peanut and sunflower oils (Gong et al., 2005; Pannu et al., 2004). In the earlier study (Pannu et al., 2004), the use of peanut oil at concentrations ranging from 2.5% to 20% (w/w) successfully removed more than 90% of anthracene (ANT) from soil at low

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contamination levels of 50 and 100 mg/kg. However, an increase in ANT concentration in soil to 1000 mg/kg resulted in a significant reduction in extraction efficiency to 15 % due to the oil saturation. The later study by Gong et al. (2005) showed that nearly all PAHs (81%-100%) were removed from a heavily contaminated former manufactured gas plant soil contaminated with a total PAH concentration of 5453.2 mg/kg. However, these high efficiencies were achieved by using a large oil:soil ratio reaching up to 4 l:1 kg. Similarly, a former study by Lau et al. (2012) using palm kernel oil (PKO) and soybean oil (SO) showed that extraction efficiencies as high as 75% were achieved with a relatively high oil: soil ratio of 10 mL:10 g.

It is evident that vegetable oil is a promising extraction agent particularly for the extraction of higher molecular weight PAHs as compared to other solvents studied (Lau et al., 2014). Nonetheless, to further advance the knowledge and utilization of vegetable oils in the field of soil remediation, one issue which must be resolved is the minimization of oils in order to justify this technology as an environmentally-friendly and cost-effective one. Thus, the present study aims to address the implications of using a multiple-stage cross-current extraction as compared to the single extraction works reported formerly in an effort to reduce the required oil volume, while maintaining high extraction efficiencies. The PKO and SO are also used in this study based on their high annual production. In addition, this study will also look into the effectiveness of an oil flotation process as a post-extraction step to remove the vegetable oil used. Experimental tests are conducted to investigate the extraction efficiencies of a 3-stage cross-current extraction of lowly and highly contaminated sand using saturated PKO and unsaturated SO compared to single extractions at 30°C and 70°C. At the optimum experimental conditions, a comparison between the extractions of highly contaminated sand and highly contaminated soil is also carried out. An oil flotation process using hot alkaline solution to remove residue oil from the treated sand/soil is also conducted and assessed as a post-extraction step. Finally, a conceptual process of the extraction of PAHs from contaminated soil using vegetable oil is proposed.

## 2. Experimental

### 2.1. Materials

Fine sand (100 % sand) was collected from an uncontaminated beach site in Port Dickson, Negeri Sembilan, Malaysia while native soil (79.0% sand, 18.5% silt, 2.5% clay) was collected from a residential area in the suburbs of Kuala Lumpur, Malaysia. The properties of both soils are shown in Table 1.

PKO was donated by Lee Palm Oil Mill, Kapar, Malaysia while SO was purchased

commercially from a local supermarket. The properties and fatty acid composition of both PKO and SO have been previously reported (Lau et al., 2012). Phenanthrene (PHEN) (technical grade, >90%) and fluoranthene (FLT) (>98%) were purchased from Sigma-Aldrich, USA. Reagent grade n-pentane, dichloromethane (DCM), methanol and n-hexane solvents (all >98 %) were purchased from Merck, Germany. Acetonitrile solvent (HPLC, Ultra Gradient Grade) was purchased from Baker, USA. ACS reagent grade (>85 %) potassium hydroxide (KOH) in pellet form and sodium carbonate anhydrous ( $\text{Na}_2\text{CO}_3$ ) were purchased from Sigma Aldrich, USA. Silica gel 40 (100/200 mesh) was purchased from Merck, Germany.

### 2.2. Spiking of soil samples

Stock solutions were produced by dissolving 1.0 g of each PAH into 100 mL of DCM to produce stock solutions. Both soil samples were air-dried and sieved to uniform consistency (< 2 mm) using an Endecott sieve. The samples were then spiked with the PHEN and FLT stock solutions to the required concentration (either 200 mg/kg or 1000 mg/kg of each PAH) and mixed thoroughly. These two representative PAHs were chosen for their different physico-chemical properties, particularly the difference in molecular weight which discriminates the two PAHs in terms of hydrophobicity, tendency for bioaccumulation, resistance to biodegradation and overall environmental persistence. The DCM was left to evaporate in a fume hood for 3 days. The original PAH concentrations in soil upon spiking was tested three times and was found to be within  $\pm 8.0$  and  $\pm 8.8\%$  of the theoretical concentrations for PHEN and FLT, respectively (Lau, 2012). This reaffirmed that the spiking protocol used was adequate. Typical of soil remediation studies using spiked soils, the theoretical concentrations were used for the determination of extraction efficiencies.

### 2.3. Single/3-stage cross-current extractions of PAH-contaminated soil

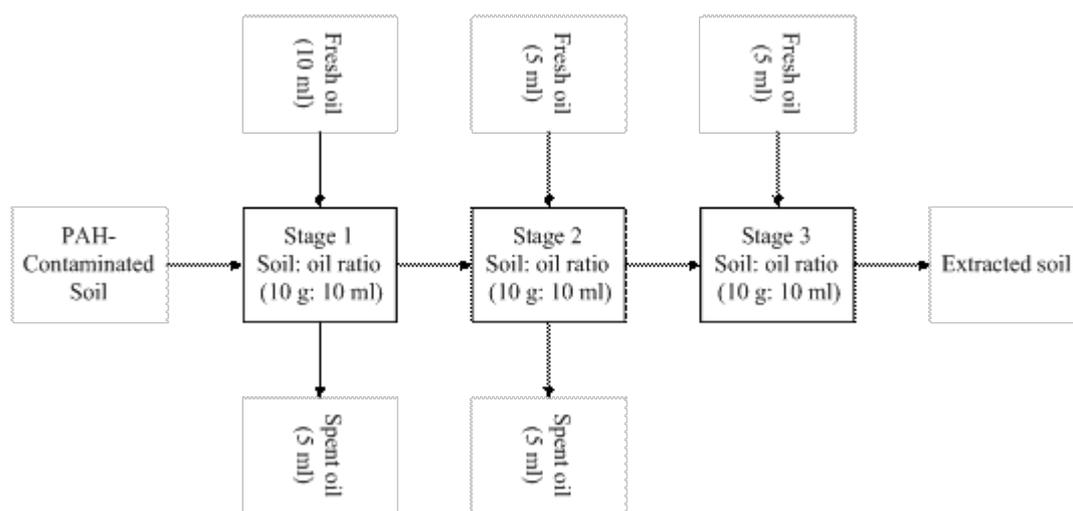
Single batch extractions with either PKO or SO were carried out in multiple Erlenmeyer flasks at an oil:soil ratio of 10 mL:10 g each in a hooded water bath with horizontal shaker (200 rpm) at temperatures of 30°C or 70°C for 24 hours.

A preliminary desorption kinetics study indicated that this duration was sufficient for equilibrium conditions to be achieved. Likewise, 3-stage cross-current extractions with either PKO or SO were also carried out at an oil:soil ratio of 10 mL:10 g each at temperatures of 30°C or 70°C for 24 hours per stage. For the second and third stages of extraction, 5 mL of contaminated oil was removed and replenished with 5 mL of fresh oil, making a total of 20 mL of oil used for the 3-stage cross-current extractions. A schematic of the 3-stage cross-current extraction is shown in Fig. 1.

**Table 1.** Properties of sand and soil samples used in this study

<i>Properties</i>		<i>Sand</i>	<i>Soil</i>
Water content (% dry weight) <sup>a</sup>		0.17 (0.02)	4.83 (0.14)
Soil Organic Matter (%) <sup>a</sup>		0.19 (0.06)	2.04 (0.16)
TOC (%) <sup>a</sup>		0.03 (0.06)	0.82 (0.02)
pH <sub>1:1 water</sub> <sup>a</sup>		7.15 (0.32)	6.47 (0.15)
Particle size distribution (% wt)	<0.106 mm	2.56 (0.25)	1.56 (0.04)
	0.106 – 0.125 mm	1.56 (0.24)	0.46 (0.02)
	0.125 – 0.25 mm	64.26 (1.55)	4.35 (0.81)
	0.25 – 0.50 mm	31.62 (1.39)	12.32 (1.09)
	0.50 – 1.00 mm	0	33.67 (1.67)
	1.00 – 1.40 mm	0	26.09 (1.16)
1.40 – 2.00 mm		0	21.56 (2.14)
Textural classification		Sand (100% sand)	Loamy sand (79.0% sand, 18.5% silt, 2.5% clay)

<sup>a</sup> Average of triplicates with standard deviation in parentheses.

**Fig. 1.** Schematic of the 3-stage cross-current extraction

The high oil viscosity prevented total oil removal after the first and second extractions. Single batch extractions with either PKO or SO at an oil:soil ratio of 20 mL:10 g were also conducted to compare the extraction efficiencies obtained with that of the 3-stage cross-current extractions. To determine the amount of PAHs extracted, one flask was sacrificed at the end of every extraction stage (24, 48 and 72 hours), and two 1 mL aliquots of oil were sampled for analysis. All extraction experiments were carried out in triplicates.

#### 2.4. Oil flotation process of soil/oil slurry with hot alkaline solution

For the oil flotation study, 50 g of sand/soil was spiked with 20 mL of vegetable oil and mechanically shaken for 6 hours at room temperature to form a homogeneous soil/oil slurry. 200 mL of distilled water was heated on a hotplate until 90°C and adjusted to a pH of 10 by the addition of Na<sub>2</sub>SO<sub>3</sub>. The hot alkaline solution was then poured into the soil/oil slurry and stirred using a magnetic stirrer at stirring speed of 125 rpm for 10 minutes. The bulk layer of froth oil that floated up during the oil flotation process was collected into a separating

flask. Upon separation, the bulk layer of oil sample was eluted into a measuring cylinder, while the remaining oil and water emulsions were centrifuged at 2000 rpm for 10 minutes. The layer of oil obtained after centrifugation was collected into a measuring cylinder using a pipette.

#### 2.5. Analytical methods

A saponification and liquid-liquid phase extraction was carried out to recover PAHs from the oil samples (Meudec et al., 2006). Firstly, the PAH-contaminated oil samples were shaken with 8 mL of methanol and 0.4 g of KOH and incubated overnight at 55°C. Then, 6 mL of n-hexane and 6 mL of distilled water was added to fractionate the extract into two phases. The upper hexane phase (insaponifiable) was passed through a silica gel 40 (100/200 mesh) glass chromatography column (6 cm x 10 mm diameter) and eluted firstly with 15 mL of n-pentane and secondly with 15 mL DCM:n-pentane (2:3, v/v). The final eluate was evaporated to dryness using a rotary evaporator and dissolved in 0.1 mL of acetonitrile for gas chromatography-flame ionization detector (GC-FID) analysis. A volume of 1 µL of the final sample was injected in splitless mode into a

Clarus 500 GC-FID (Perkin Elmer) installed with a J & W Scientific DB-5ms Ultra Inert capillary column with (5% Phenyl)-methylpolysiloxane as the stationary phase and dimensions of 30 m × 0.25 mm I.D. × 0.25 µm film thickness. The carrier gas was helium with a flow pressure of 16 psig. The temperatures at both the injector and detector ports were set at 290°C and 300°C, respectively. The oven temperature programme set for the PAH analysis was an initial temperature of 170°C for 4 min followed by 20°C/min ramp rate to a final column temperature of 270°C which was held for 4 min. The entire procedure was checked for recovery efficiencies by analysing oil samples spiked with PAH standards and the percentage recovery obtained was 86.7 (±11.2%) and 89.4 (±17.8%) for PHEN and FLT respectively from SO, and 86.9 (±13.5%) and 90.3% (±12.5%) for PHEN and FLT respectively from PKO. The experimental data was also statistically analysed using the one-way analysis of variance (ANOVA), followed by a standard one-tail *t*-test (significance level at 0.05) available in Microsoft Excel 2010.

### 3. Results and discussion

#### 3.1. Comparison of single and 3-stage cross-current extractions of LC sand and HC sand

Table 2 compares the extraction efficiencies of single extractions and 3-stage cross-current extractions of LC and HC sands. For single extractions, the efficiencies increase with increase in temperature from 30°C to 70°C. For LC sand, the extraction efficiency increases from 68.1% to 70.2%, and from 68.8% to 74.9% for PHEN and FLT, respectively using SO. Using PKO, the extraction efficiency increases from 68.2% to 71.3%, and from 69.5% to 75.3% for PHEN and FLT, respectively. Similar trends are observed in the case of HC sand.

In all tests, the PAH extraction efficiencies using PKO are higher than that of SO with differences ranging within 0.1–1.15% for LC sand and 0.78–7.99% for HC sand. The larger extraction efficiency of PKO compared to SO at 70°C could be primarily caused by the lower viscosity of PKO (Lau et al., 2012). The less viscous PKO provides better contact and wetting within the sand matrix which enhances the partitioning of PAHs into the oil phase (Walter et al., 2000). In addition, due to its lower molecular weight of 724.3 g/mol compared to 880.8 g/mol for SO, PKO possesses a larger sorption density (Yeom et al., 1996). This in effect means that PKO has better ability to sorb and penetrate into the sand matrix. The lower extraction capability of SO compared to PKO is also due to the large percentage (approximately 72% of the total fatty acid composition in SO) of bent geometric molecular structure in SO contributed by *cis* double bonds. The highly saturated PKO comprises straight-chain fatty acids which allow better access for PAH dissolution.

On a different note, it can also be observed that the extracted fractions of FLT into both oils are higher than PHEN. In particular, extraction efficiency of FLT is higher than PHEN by 4.7% and 4.0% at 70°C using SO and PKO, respectively in LC sand. Similarly in HC sand, the extraction efficiency of FLT is higher than PHEN by 2.1% and 4.4% at 70°C using SO and PKO, respectively. These observations can be attributed to the larger molecular size and molar volume of FLT which renders it more hydrophobic with a better affinity to non-aqueous phases (Lide, 2006; Zhang and Gobas, 1995; Zhou and Zhu, 2007).

An average decrease of 10.8% occurs when PAHs are extracted from HC sand compared to LC sand. This is probably caused by the larger diffusion resistance due to the increased PAH concentration which leads to an increase in temporary van der Waals interactions (dipole-dipole induced) between the PAH molecules and the low energy sorption sites on sand particles.

Referring to Table 2, the 3-stage cross-current extractions of PAH-contaminated sand significantly improve the total extraction efficiency with almost complete PAH removal from sand ( $P < 0.05$ ). Total extraction efficiencies of 86.8–92.8% and 88.6–98.0% are obtained for SO and PKO, respectively when extracted from LC sand, while total extraction efficiencies of 83.4–89.5% and 87.2–98.4% are obtained for SO and PKO, respectively when extracted from HC sand.

The 3-stage cross-current extractions significantly increase the total extraction efficiencies compared to single extractions by 18.7–22.7% and 27.2–30.6% for LC and HC sands, respectively. The renewal of vegetable oil in each extraction stage provides an increase in concentration gradient between the PAHs in the sand and the fresh oil. Furthermore, the replacement of contaminated oil with fresh oil limits re-adsorption of extracted PAHs (Strawn and Sparks, 2000; Zou et al., 2009).

A comparison with recent works of PAH extraction from soil using other extraction agents in single batch extraction is also shown in Table 3. It can be seen that the extraction efficiencies due to the renewal of SO and PKO in the 3-stage cross-current extractions presented earlier are comparable and in some cases higher than other extraction agents including organic solvent, surfactants, microemulsions, cyclodextrin, fatty acid methyl ester and biodiesel. While the extraction efficiencies using surfactants are seen to be superior with up to 94.5% extraction efficiency for PHEN (Zhao et al., 2010), it should be noted that large volumes of cosolvent are required. On a different note, Table 2 also shows the comparison of the extraction efficiencies using oil:soil ratios of 20 mL:10 g and 10 mL:10 g for both LC and HC sands. In both cases, the extraction efficiencies are not significantly improved when the volume of vegetable oil is doubled ( $P > 0.05$ ).

**Table 2.** Comparison of extraction efficiencies of single extractions and 3-stage cross-current extractions of LC and HC sand, as well as optimised extraction of HC soil

Temperature (°C)	Oil	PAH	Extraction efficiency (%)						
			LC sand			HC sand			HC soil
			Single (10mL oil:10g soil)	Single (20mL oil:10g soil)	3-stage (20mL oil:10g soil)	Single (10mL oil:10g soil)	Single (20mL oil:10g soil)	3-stage (20mL oil:10g soil)	3-stage (20mL oil:10g soil)
30	PKO	PHEN	68.2	75.6	88.6	55.4	64.2	87.2	n.a.
		FLT	69.5	77.5	90.0	60.7	68.0	92.8	n.a.
	SO	PHEN	68.1	60.2	86.8	56.3	51.6	83.4	n.a.
		FLT	68.8	68.9	87.4	59.0	55.5	85.6	n.a.
70	PKO	PHEN	71.3	75.2	96.2	63.4	68.2	94.3	82.7
		FLT	75.3	80.3	98.0	67.8	73.6	98.4	89.2
	SO	PHEN	70.2	65.7	87.9	57.6	68.2	87.1	n.a.
		FLT	74.9	72.5	92.8	59.7	73.3	89.5	n.a.

*n.a.* Data not available

**Table 3.** Comparison of extraction efficiencies of single extractions of PAHs from soil using different extraction agents

Type of extraction agent	Specific extraction agent	Soil:liquid ratio (w/v)	PAH removal (%)	Reference
Vegetable oil	Palm kernel oil	10 g:10 mL	71.3 (PHEN) 75.3 (FLT)	Lau et al. (2012)
Organic solvent	40% Ethyl lactate: 60% water (v/v)	5 g:10 mL	65 - 75 (PHEN) 58 - 67 (FLT)	Yap et al. (2012)
Surfactant	Sodium dodecyl sulphate	135 g:1800 mL	90 (PHEN)	López-Vizcaíno et al. (2012)
Surfactant	Sodium dodecylbenzenesulfonate	2 g:25 mL	81.1-94.5 (PHEN)	Zhao et al. (2010)
Surfactant	Tween 80	1 g:20 mL	55.5 (PHEN)	Zhao et al. (2005)
Microemulsions	Sodiuk castor oil sulfate microemulsion	1 g:20 mL	69.9 (PHEN)	Zhao et al. (2005)
Cyclodextrin	Hydroxypropyl-β-cyclodextrin (HPCD)	2.5 g:50 mL	70 (PHEN)	Gómez et al. (2010a)
Fatty acid methyl ester (FAME)	Synthesized from transesterification of soybean oil and methanol	5 g:5 mL	82 - 86 (PHEN)	Gong et al. (2010)
Biodiesel	Market biodiesel produced from waste cooking oil	5 g:5 mL	63 - 78 (PHEN)	Gong et al. (2010)

However, a comparison of the single extraction (20 mL) and the 3-stage cross-current extraction, both of which utilize the same total volume of oil shows a significant improvement of 1.1–1.3 times in the extraction efficiencies for the multiple stage extraction ( $P < 0.05$ ). Similar trends are also observed for HC sand. Thus, it is clear that the extraction efficiency can be significantly improved by renewing the extraction solvent in a multiple stage extraction, rather than using the same amount of extraction solvent in a single extraction, as explained earlier.

### 3.2. Performance of 3-Stage cross-current extraction of HC soil at 70°C

In both single and 3-stage cross-current extractions, maximum PAH extraction efficiency is achieved using PKO at 70°C. As such, this optimum extraction condition was employed in the extraction of HC soil to study the influence of SOM on the extraction process. From Table 2, the enhanced solubility of FLT in PKO is again observed for PAH

extraction from HC soil, with 6.5% more FLT being extracted. However, an average decrease of 10.4% in the extraction efficiencies of PAHs from HC soil is observed when compared to the extraction efficiencies of PAHs from HC sand. The total extraction efficiencies from HC soil are 11.6% lower for PHEN and 9.2% lower for FLT than previously observed extraction efficiencies from HC sand. This significant drop in extraction efficiency can be attributed to the affinity of PAHs to the SOM domains within the soil. Hydrophobic compounds such as PAHs have great affinity to both aromatic and aliphatic domains of SOM (Alvim-Ferraz et al., 2006; Haigh, 1996). The sorption of PAHs onto these SOM domains decreases their mobility and relative volatility, thus prohibiting desorption and reducing their availability for extraction (Alvim-Ferraz et al., 2006; Sun et al., 2003). In addition, it was noted that the hydrophobic organic contaminants (HOC) desorption process is dominated by SOM when SOM is present in concentrations above 0.1 % (Brusseau, 1991; Cornelisse et al., 1998). Besides the SOM content, PAHs are also suggested to be strongly

sorbed onto fine-sized particles such as the silt and clay fractions, which contributed to 18.5 % and 2.5 % of the total soil composition used in this study, as shown in Table 1 (Guerin, 1999). The clay content in soil hindered the mobility and penetration of solvent through the sample matrix, resulting in lower extraction efficiency for soil with higher clay content compared to pure sand (Elektorowicz et al., 2007).

### 3.3. Performance of oil flotation

Table 4 lists the recoveries of PKO and SO from sand and soil using the oil flotation method at 90°C with Na<sub>2</sub>CO<sub>3</sub> solution at pH 10 and stirring speed of 125 rpm. The oil recoveries from sand are 13.2–19.5% higher than soil. Averages of 90% and 88.8% are obtained for PKO and SO sand removals, respectively compared to averages of 70.5% and 75.7% for soil removals. These results can be linked to the size of sand/soil particles.

In the oil flotation process, the surface charge density of the oil/soil particles is affected upon the addition of the alkaline solution (Sonnefeld et al., 1995), resulting in an increase in the net charge of the particles and making them more repulsive. Upon the electrostatic repulsive interaction between soil and oil particles, the soil particles then slide down and finally detach themselves due to lack in buoyancy, allowing the oil droplets to float upwards due to their lighter density compared to water (Dai and Chung, 1996).

The high mechanical shear provided by agitation as well as the elevated temperature enhances the oil encapsulated gas bubbles to strip away from soil aggregates (Schramm et al., 2003). Since the soil used is largely composed of 1.0–2.0 mm particle sizes compared to the sand which is largely composed of 0.125–0.5 mm particle sizes (shown in Table 1), larger aerated droplets are formed during the oil flotation process as the size of the aerated oil droplets increases as the particle size increases (Dai and Chung, 1996). When large aerated droplets are present, the droplets stretch and become elongated, breaking into two droplets. The aerated upper portion of the break-away droplet floats to the top while the lower portion of the droplet sinks to the bottom due to the attached soil particles. Thus, the amount of oil recovered from the flotation of soil/oil slurry is reduced compared to the amount of oil recovered from the sand/oil slurry.

### 3.4. Feasibility of vegetable oil as extracting agent for PAHs

This study highlights the feasibility of using vegetable oils to remove PAHs from soil. The results obtained here indicate that PKO or highly saturated oils are better solvents for PAH removal from soils. On a pilot - or field- scale, the temperature and number of extraction stages will need to be adjusted depending on the level of contamination and the required level of detoxification. The use of a single stage compared to more stages with the same total volume of solvent is not recommended due to the resulting lower extraction efficiencies. Nonetheless, the higher extraction efficiencies afforded by increased temperatures and extraction stages are accompanied by higher capital/operating costs. A techno-economic study on a pilot-scale is hence necessary to provide a reliable cost estimation of this remediation approach.

One of the advantages of using vegetable oil as shown here is that higher molecular weight (HMW) PAHs have better affinity and larger solubility in vegetable oil compared to lower molecular weight (LMW) PAHs. This can be considered as the prime advantage of using oils. Moreover, the capability of oils in removing large fractions of HMW PAHs in soil will significantly improve the soil quality since the carcinogenicity and toxicity of PAHs increase with increasing molecular size.

Due to the affinity of PAHs to SOM domains resulting in reduced extraction efficiencies, the use of vegetable oil to remove PAHs is best employed in low SOM soils/sands. A conceptual process of the extraction of PAHs from contaminated soil using vegetable oil is proposed as shown in Fig. 2. The bulk vegetable oil removed via filtration as well as the recovered vegetable oil from the oil flotation process can be regenerated by the absorption process using activated carbon. The recovered oil can be used again for the PAH extraction, while the spent activated carbon can then be disposed off via incineration or landfill.

## 4. Conclusions

The maximum extraction efficiency of 94.3% and 98.4% for PHEN and FLT, respectively can be achieved via a 3-stage stage cross-current extraction using PKO at 70°C.

**Table 4.** Oil recovery from sand and soil using oil flotation (oil:soil ratio of 20 mL:50 g, pH 10, and stirring speed 125 rpm)

Soil	Oil	Oil recovery (%) <sup>a</sup>	Remaining oil volume in soil (mL)	Oil residue in soil (% v/w)
Sand	PKO	90.0 (1.32)	2.0	4.0
	SO	88.8 (1.76)	2.2	4.5
Soil	PKO	70.5 (3.50)	5.9	11.8
	SO	75.7 (5.30)	4.9	9.7

<sup>a</sup>The oil recovery percentages are averages of triplicated with standard deviations in parenthesis.

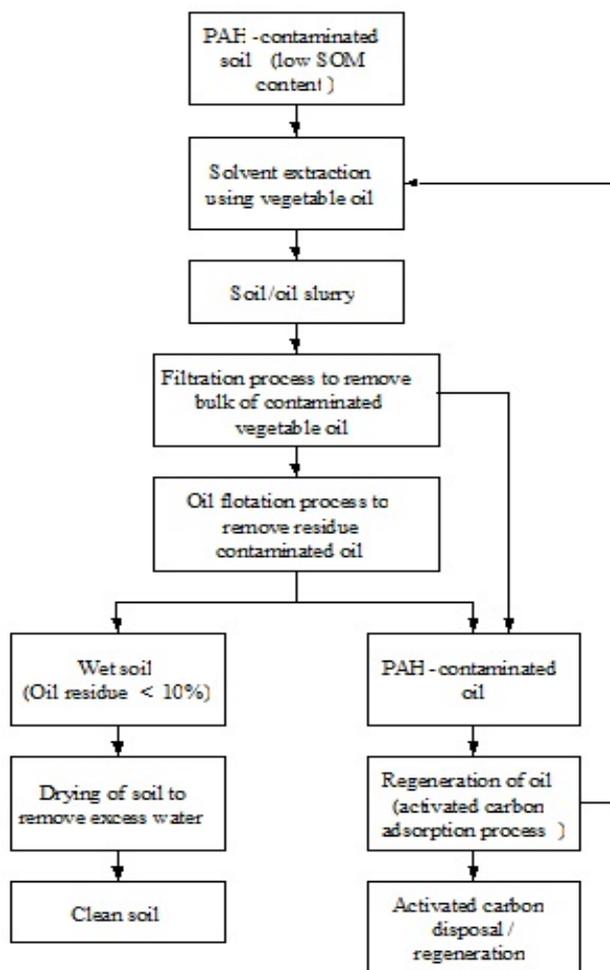


Fig. 2. Proposed scheme for the extraction of PAHs from contaminated soil using vegetable oil

For LC sand, total extraction efficiencies of 86.8–92.8% and 88.6–98.0% are obtained for SO and PKO, respectively. For HC sand, total extraction efficiencies of 83.4–89.5% and 87.2–98.4% are obtained for SO and PKO, respectively. Extraction efficiencies of PAHs from HC soil using PKO at 70°C as observed from 3-stage cross-current extractions, decrease compared to HC sand. An oil flotation process as a post treatment step for soil/oil slurry has been demonstrated to successfully remove residue oil from treated soil.

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#### References

Alvim-Ferraz M.C.M., Albergaria J.T., Delerue-Matos C., (2006), Soil remediation time to achieve clean-up Goals II: influence of natural organic matter and water contents, *Chemosphere*, **64**, 817-825.  
 Brusseau M.L., (1991), Cooperative sorption of organic chemicals in systems composed of low organic carbon aquifer materials, *Environmental Science and Technology*, **25**, 1747-1752.

Cornelissen G., van Noort P.C.M., Govers H.A.J., (1998), Mechanism of slow desorption of organic compounds from sediments: a study using model sorbents, *Environmental Science and Technology*, **32**, 3124-3131.  
 Dai Q., Chung K.H., (1996), Hot water extraction process mechanism using model oil sands, *Fuel*, **75**, 220-226.  
 Elektorowicz M., El-Sadi H., Lin J., Ayadat T., (2007), Effect of supercritical fluid extraction parameters and clay properties on the efficiency of phenanthrene extraction, *Journal of Colloid and Interface Science*, **309**, 445-452.  
 Gan S., Lau E.V., Ng H.K., (2009), Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs), *Journal of Hazardous Materials*, **172**, 532-549.  
 Guerin T.F., (1999), The extraction of aged polycyclic aromatic hydrocarbon (PAH) residues from a clay soil using sonication and a Soxhlet procedure: a comparative study, *Journal of Environmental Monitoring*, **1**, 63-67.  
 Gómez J., Teresa Alcántara M., Pazos M., Ángeles Sanromán M., (2010), Soil washing using cyclodextrins and their recovery by application of electrochemical technology, *Chemical Engineering Journal*, **159**, 53-57.  
 Gong Z., Alef K., Wilke B.-M., Li P., (2005), Dissolution and removal of PAHs from a contaminated soil using sunflower oil, *Chemosphere*, **58**, 291-298.

- Gong Z., Wang X., Tu Y., Wu J., Sun Y., Li P., (2010), Polycyclic aromatic hydrocarbon removal from contaminated soils using fatty acid methyl esters, *Chemosphere*, **79**, 138-143.
- Hyman M., Dupont R.R., (2001), *Groundwater and Soil Remediation: Process Design and Cost Estimating of Proven Technologies*, ASCE Press, Virginia, USA.
- Lau E.V., (2012), *Extraction of Polycyclic Aromatic Hydrocarbons (PAHs) from Contaminated Soil using Vegetable Oil*, PhD Thesis, University of Nottingham Malaysia Campus, Malaysia.
- Lau E.V., Gan S., Ng H.K., (2012), Extraction of phenanthrene and fluoranthene from contaminated sand using palm kernel and soybean oils, *Journal of Environmental Management*, **107**, 124-130.
- Lau E.V., Gan S., Ng H.K., Poh P.E., (2014), Extraction agents for the removal of polycyclic aromatic hydrocarbons (PAHs) from soil in soil washing technologies, *Environmental Pollution*, **184**, 640-649.
- Li H., Chen J., Shi Z., (2016), PAH removal efficiency in surfactant-enhanced soil washing systems: influence of Pah ring number and soil properties, *Environmental Engineering and Management Journal*, **15**, 1665-1672
- Lide D.R., (2006), *CRC Handbook of Chemistry and Physics*, 87<sup>th</sup> Edition, CRC Press, Taylor & Francis Group, Florida, United States of America.
- López-Vizcaíno R., Sáez C., Cañizares P., Rodrigo M.A., (2012), The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment, *Separation and Purification Technology*, **88**, 46-51.
- Meudec A., Dussauze J., Deslandes E., Poupart N., (2006), Evidence for bioaccumulation of PAHs within internal shoot tissues by a halophytic plant artificially exposed to petroleum-polluted sediments, *Chemosphere*, **65**, 474-481.
- Pannu J.K., Singh A., Ward O.P., (2004), Vegetable oil as a contaminated soil remediation amendment: application of peanut oil for extraction of polycyclic aromatic hydrocarbons from soil, *Process Biochemistry*, **39**, 1211-1216.
- Savić R., Radović J.R., Ondrašek G., Pantelić S., (2016), Occurrence and sources of polycyclic aromatic hydrocarbons (PAHs) in drainage channel sediments in Vojvodina (Serbia), *Environmental Engineering and Management Journal*, **15**, 287-295.
- Schramm L.L., Stasiuk E.N., Turner D., (2003), The influence of interfacial tension in the recovery of bitumen by water-based conditioning and flotation of Athabasca oil sands, *Fuel Processing Technology*, **80**, 101-118.
- Sonnefeld J., Göbel A., Vogelsberger W., (1995), Surface charge density on spherical silica particles in aqueous alkali chloride solutions, Part 1. Experimental results, *Colloid Polymer Science*, **273**, 926-931.
- Strawn D.G., Sparks D.L., (2000), Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil, *Soil Science Society of America Journal*, **64**, 144-156.
- Sun H., Tateda M., Ike M., Fujita M., (2003), Short- and long-term sorption/desorption of polycyclic aromatic hydrocarbons onto artificial solids: effects of particle and pore sizes and organic matters, *Water Research*, **37**, 2960-2968.
- Walter T., Ederer H.J., Först C., Stieglitz L., (2000), Sorption of selected polycyclic aromatic hydrocarbons on soils in oil-contaminated systems, *Chemosphere*, **41**, 387-397.
- Wild S.R., Jones K.C., (1995), Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget, *Environmental Pollution*, **88**, 91-108.
- Yap C.L., Gan S., Ng H.K., (2010), Application of vegetable oils in the treatment of polycyclic aromatic hydrocarbons-contaminated soils, *Journal of Hazardous Materials*, **177**, 28-41.
- Yap C.L., Gan S., Ng H.K., (2012), Evaluation of solubility of polycyclic aromatic hydrocarbons in ethyl lactate/water versus ethanol/water mixtures for contaminated soil remediation applications, *Journal of Environmental Sciences*, **24**, 1064-1075.
- Yeom I.T., Ghosh M.M., Cox C.D., (1996), Kinetic aspects of surfactant solubilization of soil-bound polycyclic aromatic hydrocarbons, *Environmental Science and Technology*, **30**, 1589-1595.
- Zhang X., Gobas F.A.P.C., (1995), A thermodynamic analysis of the relationships between molecular size, hydrophobicity, aqueous solubility and octanol-water partitioning of organic chemicals, *Chemosphere*, **31**, 3501-3521.
- Zhao B., Zhu L., Gao Y., (2005), A novel solubilization of phenanthrene using Winsor I microemulsion-based sodium castor oil sulfate, *Journal of Hazardous Materials*, **B119**, 205-211.
- Zhao Q., Weise L., Li P., Yang K., Zhang Y., Dong D., Li P., Li X., (2010), Ageing behavior of phenanthrene and pyrene in soils: A study using sodium dodecylbenzenesulfonate extraction, *Journal of Hazardous Materials*, **183**, 881-887.
- Zhou W., Zhu L., (2007), Efficiency of surfactant-enhanced desorption for contaminated soils depending on the component characteristics of soil-surfactant-PAHs system, *Environmental Pollution*, **147**, 66-73.
- Zou Z., Qiu R., Zhang W., Dong H., Zhao Z., Zhang T., Wei X., Cai X., (2009), The study of operating variables in soil washing with EDTA, *Environmental Pollution*, **157**, 229-236.